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Principles of Polymer Networking and Gel Theory in Thermosetting Adhesive Formulations

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I. INTRODUCTION

The study of adhesion and adhesives involves many scientific approaches and in particular many different scientific disciplines. From physics to applied engineering, from surface science to chemistry, be it analytical, organic, or physical, all have, and would have a contribution to make to the fields of adhesives and adhesion. Polymer science is, among others, one of the important ways to approach several fields of the science of adhesives. However, while polymer physics and perhaps the physical chemistry of polymers are extensively used in this field, not much work is found that reports the use of the principles of polymer chemistry and, in particular, of polymer networking and gelation theory in the applied formulation of adhesives, i.e. on how adhesives are made to achieve particular effects. While in many other fields this branch of science is used extensively, in adhesive formulation a variety of factors have contributed to the lack of its extensive use. The main cause of this is the relative unwillingness of this industry to abandon empirical research, this being an approach often successful in solving some applied adhesive problems. Notwithstanding this, important applicable results can be rapidly achieved from polymer gel theory if this science is properly applied to adhesive formulation, and these results are obtainable much more readily and with much less effort than by empirical research.

So, in this chapter the interest and importance of the polymer gel theory approach to the formulation of adhesives will be briefly shown and, in particular, we will limit this to thermosetting wood adhesives obtained by polycondensation such as phenol–formaldehyde-, urea–formaldehyde-, melamine–formaldehyde- and resorcinol–formaldehyde-based adhesives. The same approach is, however, very valid for other polycondensation resins, and also for adhesives obtained by routes other than polycondensation.

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II. SOME PRINCIPLES OF POLYMER NETWORKING AND GEL THEORY OF IMPORTANCE TO THERMOSETTING ADHESIVES

Several theories and methods defining and modeling the formation of polymer networks exist [1–3]. The most useful of such theories, purely from an applied everyday use, are often the simpler and older ones [4,5]. More complex theories, although often excellent at describing to a much greater and thorough extent the molecular reality of gelation, suffer also from being rather difficult to use and unyielding for everyday practice. Thus, they often remain rather unapprochable to those who could benefit most from their application for the easy resolution of applied problems.

Many such theories concentrate on the determination, by different mathematical approaches and different physicochemical approximations, of the degree of conversion and hence of the advancement of polymerization at the point of gel formation and on the calculation of basic polymer parameters derived from the determination of the gel point. Two main approaches are used: statistical methods and kinetic methods. Combinations of the two have also been presented [1].

A. Statistical Methods

These methods generate structures by random combinations of reacting functional groups. This approach is thorough and the results are good when dealing with equilibrium-controlled reactions. The results are often a good approximation in kinetic-controlled reactions. Most of the formaldehyde-based polycondensations are equilibrium-controlled reactions, this being particularly true for urea–formaldehyde, melamine–urea–formaldehyde, phenol–formaldehyde and phenol–resorcinol–formaldehyde adhesive resins. Statistical methods are then ideal to describe these adhesive systems at the moment of gel formation and during formation of the hardened network.

Among the statistical method dealing with polymer networking and gelation in the field of polycondensation must be considered:

(1) The gel theory of Carothers [4] in which the critical degree of conversion at the gel point (p_{gel}) is defined as $p_{gel} = 2/f$, with f being the average functionality of the monomers in the system.
(2) The probabilistic gel theory of Flory [5]–Stockmayer [6,7] in which p_{gel} is defined through the coefficient of branching $\alpha = 1/(f-1)$. In this theory f is taken as the functionality of the monomer of greater functionality. The main expression of this theory is the equation $\alpha = rp^2\rho/[1 - rp^2(1-\rho)]$ where p is both the degree of conversion and the probability that a certain reactive group type has in fact reacted, ρ is the proportion of such a reactive group type belonging to branching units, and r is the ratio of the types of reactive groups of the two monomers participating in the polycondensation.
(3) The cascade process theory of Gordon [8,9] based on more complex functions than the two preceding ones but also offering some further advantages over them.
(4) The Miller–Macosko [10] recursive method.
(5) The stochastic graphes theory of Bruneau [11] which is a more complete theory but very complex and complicated to use.

Even more complex theories can be found in the review literature [2,3]. Of the above theories the first two are of such a simplicity to be constantly used and the third and fourth

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ones are also used sometimes. They all suffer from some drawback: the Carothers theory, for instance, overestimates the numerical value of p_{gel} while Flory's theory underestimates it, but they are nonetheless extremely useful in solving applied problems. Furthermore, they do not describe what happens in the system between reaching the gel point and complete hardening of the network.

Percolation is another technique that is also used for structure growth simulation. Percolation techniques are only statistical methods of a slightly differently nuanced approach, and they appear not to be very suitable general methods to correlate structure and structure growth parameters but seem to be useful in examining structure growth near the gel point.

B. Kinetic Methods

Kinetic or coagulation theories develop all chemical species by the use of an infinite set of kinetic differential equations [1]. The resulting chemical species distribution can be obtained analytically only in the simplest case of random reactions; in some other cases distributions can be obtained numerically; and lastly the solution of the set of equations can also be obtained by Monte Carlo simulation methods. The application of kinetic methods has severe disadvantages: the gel is considered as one giant molecule, and hence cannot generate parts of the structures which are characteristic of the gel; and the equations and methods used are long, unyielding, and not very handy or practical to use. Combination of statistical and kinetic theories in some rare cases solves the problems inherent to the kinetic approach alone. Combination of statistical and kinetic theories also results in systems even more complex and unyielding that kinetic theory treatments alone. This field is not a very successful one. However, it is also in this field that the trend to ever more unwieldy mathematical treatment systems has led to approaches bordering on meaninglessness [12–14]. These are exercises removed from reality [12–14]. These have been developed for many years by groups [12–14] which have not understood that the aim of theories in this field is not to render more difficult but rather to solve everyday applied problems. Not only it is inconvenient to carry around equations half a page or longer as advocated by these groups, but their results cannot be believed either. Thus, these unwieldy methods are not worth further mention here.

C. Simple Statistical Gel Theories

The branching coefficient as defined by Flory is $\alpha =$ the probability that a certain branched unit will be joined to a second branched unit rather than to a terminal group. For example, for a trifunctional monomer if $\alpha = 1/2$ the molecule is a continuous chain equivalent in theory to a gel. In this case $\alpha = 1/2$ is the critical condition defining the start of the formation of an infinite tridimensional network.

When the monomer has functionality greater than or equal to 3 the system will gel when $\alpha(f-1) > 1$. The critical value of α is then

$$\alpha = \frac{1}{f-1} \tag{1}$$

where in Flory's statistical gel theory α is $=$ the functionality of the monomer of higher functionality when there are only two monomers taking part in the polycondensation reaction. So if $f=3$ then $\alpha=0.5$. If $f=4$ then $\alpha=0.33$, etc. When $\alpha=0$ there is no reaction and when $\alpha \geq 1$ the system never gels. The gel point of a thermosetting resin, hence of an

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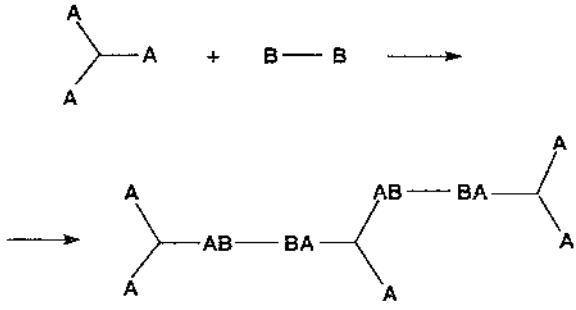
adhesive based on a thermosetting resin, depends on

1. the functionality of the monomers
2. the degree of conversion reached by the reaction
3. the ratio of the two monomers, or more exactly of the reactive sites/groups of the two monomers.

1. *Case 1: Case of Reaction of a Trifunctional Monomer with a Bifunctional Monomer*

In the polycondensation of a trifunctional monomer with a bifunctional monomer



the limiting condition to gelling is then that a bifunctional B–B monomer must be linked to two branched monomers, hence bound to two trifunctional monomers. Thus, if the proportion of B–B is limited, the extent of branching is also limited. The limiting condition to start branching, hence for the start of gelling, depends on the probability that segments –AB–BA– do indeed exist. In the theory all groups are considered as they cannot react with groups of the same kind (thus A can only react with B) and all groups have the same reactivity: the probability that the first group A (the one on the left) has then reacted with a group B is p_A, namely the fraction of all the groups A which have reacted. The probability that the second group B (the one on the right) has reacted with a group A is then p_B. The probability then that the segment –AB–BA– occurs is

$$p_A\, p_B$$

therefore

$$\alpha = p_A\, p_B \tag{2}$$

which is the probability of a joint between two branching sites. As the functionality of the monomer of higher functionality in this example has been taken as $f = 3$ then $\alpha = 0.5$. this means that at the gel point

$$(p_A\, p_B)_{gel} = \alpha \tag{3}$$

As the initial concentrations of reactive groups A and B are considered here to be the same, then $p_A = p_B = p$ and hence

$$p_{gel}^2 = \alpha \qquad \text{and} \qquad p_{gel} = \alpha^{1/2} \tag{4}$$

Which gives

$$p_{gel} = 0.707 \tag{5}$$

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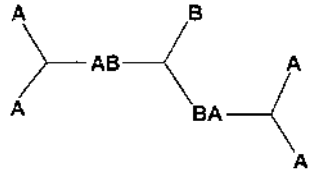
Where p_{gel} is the degree of conversion at the gel point which means that 70.7% of the reactive groups/sites of the system have reacted at the gel point.

2. *Case 2: Case of Two Trifunctional Monomers*

The polycondensation of two trifunctional monomers



In this case it is necessary that an –AB– joined segment exists between branching sites. This is equivalent to saying that

$$\alpha = p_A \quad \text{or} \quad p_B \quad \text{(depending which one is less)} \tag{6}$$

when A and B are at the same initial concentration. Thus, $p_A = p_B = p$, and the limiting condition for a gel to form will be

$$\alpha = p \tag{7}$$

Because here too $f = 3$ and $\alpha = 0.5$, the limiting condition for a gel to form will then be

$$p_{gel} = 0.5 \tag{8}$$

Where p_{gel} is the degree of conversion at the gel point which means that 50% of all the reactive groups/sites of the system have reacted at the gel point.

These two cases are valid also for monomers of higher functionality with the provision that higher functionality means a different value of f, hence a different value of α. Thus, in the case of polycondensations based only on two monomers there are only two possible cases to consider, one in which a bifunctional monomer is also present, and the other in which only monomers of functionality greater than or equal to 3 are present in the reaction medium. To take into account the cases in which the reactive sites of the two molecules are not equimolar one can define a ratio r as the ratio of the number of reactive sites A and B, with the proviso that r must always be smaller than or equal to 1 (so, if A > B $r = B/A$ and vice versa if A < B $r = A/B$; If r is greater than 1, absurd results are obtained and the theory cannot be used) [15]. The simpler form of the equations defined by Flory to describe the two cases above are then

$$p_{gel} = \left(\frac{\alpha}{r}\right)^{1/2} \qquad \text{with} \qquad r = \frac{N_A}{N_B}$$

and

$$p_{gel} = \frac{\alpha}{r} \tag{9}$$

These equations are in their simplest usable form. The original equations of Flory took into account also the density of the hardened polymer. It has been disregarded here as it is of no consequence in the formulation of thermosetting adhesives discussed later.

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3. *Case 3: Case of Many Mono-, Bi-, Tri-, and Multifunctional Monomers*

The equations described in the previous two cases are not applicable to polycondensation systems in which either monofunctional monomers are present or a great number of branching monomers of a number of different functionalities of both type A and B are present. If one considers the most general case of a polycondensation system as

$$A + A_2 + A_3 + \cdots + A_i + B + B_2 + B_3 + \cdots B_j \rightarrow \text{polymer network}$$

in which are present: (1) monomers the functionality of which is between 1 and i for the reactive groups A, and (2) monomers the functionality of which is between 1 and j for the reactive groups B, the degree of conversion and advancement of the polycondensation reaction at the gel point is given by the following equation [15–17]:

$$p_{\text{gel}} = \frac{1}{[r(f_{\mathbf{A}} - 1)(f_{\mathbf{B}} - 1)]^{1/2}} \tag{10}$$

where f_{A} and f_{B} are the weighted average functionalities of the reactive molecules A and B respectively, and where r is the same as above and represents the difference in stochiometric proportions of the reactive sites. f_{A} and f_{B} are defined as

$$f_{\text{A}} = \frac{\Sigma f_{\text{A}i}^2 N_{\text{A}i}}{\Sigma f_{\text{A}i} N_{\text{A}i}} \qquad \text{and} \qquad f_{\text{B}} = \frac{\Sigma f_{\text{B}j}^2 N_{\text{B}j}}{\Sigma f_{\text{B}j} N_{\text{B}j}} \tag{11}$$

where $N_{\text{A}i}$ are the number of moles of Ai containing $f_{\text{A}i}$ functional groups for each A-type molecule. The use of these equations is better shown by an example. Thus, for the following complex system of reagents

4 mol A	2 mol B
51 mol A_2	50 mol B_2
2 mol A_3	3 mol B_3
3 mol A_4	3 mol B_5

$$r = \frac{1(4) + 2(51) + 3(2) + 4(3)}{1(2) + 2(50) + 3(3) + 5(3)} = 0.9841$$

$$f_{\text{A}} = \frac{[1^2(4) + 2^2(51) + 3^2(2) + 4^2(3)]}{[1(4) + 2(51) + 3(2) + 4(3)]} = 2.2097$$

$$f_{\text{B}} = \frac{[1^2(2) + 2^2(50) + 3^2(3) + 5^2(3)]}{[1(2) + 2(50) + 3(3) + 5(3)]} = 2.4127$$

$$p_{\text{gel}} = \frac{1}{[0.9841(1.2097)(1.4127)]^{1/2}} = 0.7711$$

This indicates that in such a complex polycondensation system gelling occurs when 77.11% of the reagents have in fact reacted. Equation (10) is then particularly useful when using Flory's statistical theory of gelation. Owing to its simplicity and ease of use, Flory's theory of gelation is the most useful theory to use for the formulation of thermosetting polycondensation adhesives. Flory's theory presents, however, a problem: it underestimates the degree of conversion at the gel point by around 10%. This means that an experimental value of $p_{\text{gel}} = 0.770$ corresponds to a calculated value of $p_{\text{gel}}(\text{Flory}) = 0.700$–$0.710$. This is due to not being able to take into consideration cyclization reactions, a fact established by Stockmayer, so this theory is often known today as the Flory–Stockmayer gelation theory.

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Other theories, however, do exist, but the majority of these were published well after Flory's. These theories became increasingly complex and notwithstanding that they allowed perhaps a somewhat better precision in the determination of p_{gel}, the equations derived from them are so complex that in practice they are never used. This unnecessary complexity trend has gotten out of hand in certain cases to the level of a purely mathematical exercise rather removed from reality [12–14].

However, a second theory, older than Flory's, does indeed exist. This is the theory of Carothers. According to Carothers

$$\overline{\mathrm{DP}}_n = \frac{2}{2 - \bar{f}p} \tag{12}$$

where $\overline{\mathrm{DP}}_n$ is the number-average degree of polymerization and $\bar{f}$ is the average functionality of the system (a concept different from that of Flory's) which is equal to

$$f = \frac{[N_A f_A + N_B f_B]}{[N_A + N_B]} \tag{13}$$

where N_A and N_B are the numbers of moles of monomers A and B, and f_A and f_B are the functionalities, respectively, of monomers A and B. The degree of conversion in this theory is defined by the equation of Carothers

$$p = \left(\frac{2}{f}\right)\left[1 - \left(\frac{1}{\mathrm{DP}_n}\right)\right] \tag{14}$$

Because DP_n becomes very large at the gel point as p tends to $2/f$, the critical condition for gelling is defined in the Carothers equation as

$$p_{gel} = \left(\frac{2}{f}\right) \tag{15}$$

While the theory of Flory underestimates the gel point, the theory of Carothers overestimates it. For example, for the case of a trifunctional and bifunctional reaction system presented above, at equimolar reactive groups, while Flory's theory forecasts $p_{gel} = 0.707$, Carothers theory forecasts a value of $p_{gel} = 0.833$, while the experimental p_{gel} is 0.765–0.775. Recently, however [18,19], thermodynamic reasons why the two formulas should be combined came to light. This led to the proposal of a very simple equation affording much higher precision than each theory alone. This simple equation also gave much better precision of all the very complex and difficult to use theories devised and presented since Flory's 1942 one:

$$p_{gel} = \frac{(2/\bar{f}) + (\alpha/r)^{1/2}}{2}$$

or

$$p_{gel} = \frac{1}{\bar{f}} + \frac{1}{2}\left(\frac{\alpha}{r}\right)^{1/2} \tag{16}$$

This equation is nothing other than the average of the equations of Carothers and Flory, and for instance yields a $p_{gel} = 0.770$, while the most exact of the complex theories yields a $p_{gel} = 0.800$ [18,19] for the simple case just shown above. The 1/2 operator is not there (but α/r is) in the case where no bifunctional monomer is present. This is valid also for the generalized Eqs. (17) and (18) which follow and which have been developed from Eq. (16) above. For two monomers, Eq. (16) can be developed to eliminate the presence in the

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equation of two different ways of expressing functionality [Carothers' average functionality of the system in the same equation in which appears (hiding in α) Flory's functionality]. Equation (16) can then be expressed in the same functionality, so as to eliminate such a discrepancy.

$$p_{\text{gel}} = \frac{n_A + n_B}{f_A n_A + f_B n_B} + \frac{1}{2}\left(\frac{f_B n_B}{f_A n_A (f_A - 1)}\right)^{1/2} \tag{17}$$

In the case of a system of more than two monomers where each monomer can react with the other but not with itself the general formula becomes

$$p_{\text{gel}} = \frac{\Sigma n_x}{\Sigma n_x f_x} + \frac{1}{2}\left(\frac{\alpha}{\Sigma r_x + \Sigma r_{xy}}\right)^{1/2} \tag{18}$$

In the most common case in thermosetting polycondensation adhesives, namely a reaction system composed of three monomers in which two can both react with the third one but where the former two cannot react with each other (and no monomer can react with itself), the equation for higher precision determination of the degree of conversion at the gel point becomes

$$p_{\text{gel}} = \frac{\Sigma f_x n_x}{\Sigma n_x} + \left(\frac{\alpha}{\Sigma r_x}\right)^{1/2} \tag{19}$$

It is easy to see from these equations that these higher precision equations become rapidly more difficult to use and to handle as the polycondensation system becomes more complex. Thus, Eq. (16) for two-reagent systems is used very easily, and Eq. (19) for three-reagent systems is still relatively easy to use, but for more complex systems Eq. (10) [15–17] is easier to use notwithstanding the 10% lower value it gives.

III. EXAMPLES OF APPLICATIONS TO THERMOSETTING WOOD ADHESIVES

A. Formulation of Phenol–Resorcinol–Formaldehyde Cold-Set Adhesives

Resorcinol-based adhesives are used extensively to bond structural grade, exterior laminated beams for building construction (see Chap. 29 on Resorcinol Adhesives). The cold-setting adhesives which dominate this field are based on phenol–resorcinol–formaldehyde (PRF) resins. The adhesive itself is composed of the PRF resin and a hardener that includes formaldehyde, often in the form of paraformaldehyde mixed with inert fillers. The performance of the resin is resorcinol dependent. The cost of the resin is also resorcinol dependent as this is a very expensive chemical produced industrially in only three locations in the world. The research work on these resins from their inception has then been based on the optimization of their bonding performance coupled with the decrease in the relative percentages of resorcinol used. It has the been a long and successful work of empirical research and development which still continues.

It is, however, simpler to calculate from basic principles of polycondensation gel theory, hence using polymer chemistry, the relative amount of resorcinol which needs to be used in the preparation of a certain PRF resin to optimize its performance. As a simplified real example of the approach, let us propose the following problem.

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Let us assume that we have prepared a linear phenol–formaldehyde (PF) resol resin of number average degree of polymerization $\overline{DP}_n = 2$ and average content of hydroxybenzyl alcohol (methylol) $-CH_2OH$ groups of 2. If one wants to prepare a PRF cold-set adhesive for wood laminated beams or fingerjointing, how can one determine the minimum quantity of expensive resorcinol which is needed to make sure that the addition does not gel the resin? Such a problem in short asks what is the minimum amount of resorcinol one needs to have a good performance resin which does not gel on resorcinol addition to the reaction. A resin that is taken as hardening only on addition of further formaldehyde hardener, but only in the glue mix.

According to Eqs. (1)–(4) to assure that the resin system does not gel on addition of resorcinol one imposes the limiting condition

$$p_{\text{gel}}(\text{experimental}) \geq 1 \tag{20}$$

As Flory's version of the polycondensation gel theory, which we will use for this problem, underestimates by approximately 10% the degree of conversion p at the gel point this means that the limiting condition expressed by Eq. (20) can be written using Flory's theory as

$$p_{\text{gel}}(\text{Flory's}) \geq 0.9 \tag{21}$$

As the functionality of resorcinol is 3 (three potential reactive sites) and of the PF resol resin is 2 (namely two reactive $-CH_2OH$ groups) this means that Flory's branching coefficient $\alpha = 1/(f-1) = 1\,(3-1) = 0.5$, and because from Eq. (9) $p_{\text{gel}}^2 = \alpha/r$ one can write numerically the limiting condition defined by the problem as:

$$(0.9)^2 = \frac{0.5}{r} \tag{22}$$

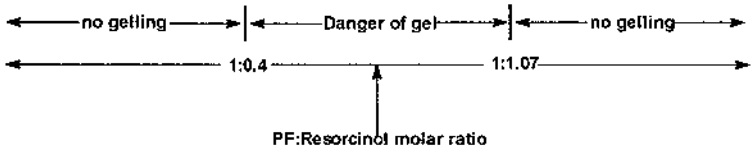
one obtains from this a value of $r = 0.617$. Consequently, because $1\,\text{mol PF} = 2\,\text{mol}$ $-CH_2OH$ and $1\,\text{mol resorcinol} = 3\,\text{mol}$ reactive sites:

$$\left(\frac{2}{3}\right)x = r \tag{23}$$

hence $(2/3)x = 0.617$ and the unknown variable $x = 0.93$. This means then that 0.93 moles of PF are needed for each mole of resorcinol, which is the equivalent to saying that the PF: resorcinol molar ratio $\geq$ 1:1.07 is needed.

However, $(3/2)x = r = 0.617$ is an equally valid situation (as r is still maintained lower than 1). Solving this equation one obtains $x = 0.411$. This means that there will be no gelling of the resin system when adding less than 0.411 mol resorcinol to each mol PF resin, thus when the PF:resorcinol molar ratio is ≤ 0.411.

This means then



It is then easy to determine by polymer chemistry calculations what should be the most adequate amount of resorcinol which needs to be added to a PF resin to obtain a

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PRF. Three types of back-checks are, however, needed, namely:

(i) To check mathematically that the assumption that has been imposed at the beginning, p_{gel} (Flory's) ≥ 0.9, is indeed correct. The 1.07 mol resorcinol is equal to $1.07 \times 3 = 3.21$ mol resorcinol reactive sites. According to Flory's Theory in the most simple form $p_{gel} = (\alpha/r)^{1/2}$, and as $\alpha = 0.5$ and $r = 2/3.21 = 0.623$, $p_{gel} = 0.896$. This is sufficiently close to the value of 0.9 which was imposed on the system at the beginning. It is then not necessary to repeat the calculation. Had this value been further from the initial 0.9 assumption a second iteration could have been done by imposing as a new starting hypothesis p_{gel}(Flory's) $\geq$ the new value found (here 0.896), until a sufficiently stable value and condition has been found by iteration.

(ii) Visual check: what does it really mean that amounts of resorcinol lower than 0.411 mol and greater than 1.07 mol stop the system from gelling (until a hardener is added), and how can this be visualized? When the amount of resorcinol is between 0.411 mol and 1.07 mol there is sufficient resorcinol for two or more $-CH_2OH$ methylol groups from separate PF resol chains to condense on the resorcinol nuclei. This leads to the formation of a three-dimensional network sufficiently large to yield a gel: the resorcinol functions then as the "hardener" for the PF resol resin, as shown by the following schematic figure:

$$-CH_2-(\text{Phenol}-CH_2)_n-\underset{\displaystyle CH_2-(\text{Phenol}-CH_2)_n-}{\overset{\displaystyle |}{\text{R}}}-CH_2-(\text{Phenol}-CH_2)_n-$$

When instead the amount of resorcinol ≥ 1.07 mol the majority of $-CH_2OH$ methylol groups have each mainly (but not only) reacted with one resorcinol molecule. Thus, there are no more methylol groups available for reaction, if one had nearer to 2 mol resorcinol to 1 mol for the particular PF at hand. At best one methylol group reacts with one resorcinol, for example

$$\text{R}-CH_2-(\text{Phenol}-CH_2)_n-\text{R} \qquad \text{and} \qquad \text{R}-CH_2-(\text{Phenol}-CH_2)_n-\text{R}$$

In reality the situation that presents itself is as follows

$$-CH_2-(\text{Phenol}-CH_2)_n-\text{R}-CH_2-(\text{Phenol}-CH_2)_n-\text{R}$$

and

$$\text{R}-CH_2-(\text{Phenol}-CH_2)_n-\text{R}-CH_2-(\text{Phenol}-CH_2)_n-$$

This is closer to the real situation, in which PRF oligomers are formed but there is enough resorcinol present to stop the oligomers growing to too long a polymer, hence to gel. If viscosity is too high, some unreacted resorcinol is added to decrease the average molecular mass of the system. This brings the system viscosity down to a more acceptable level. No interactions are possible unless a hardener (generally additional formaldehyde) is added. This means that, in the absence of a hardener, bridges between two resorcinol nuclei grafted onto PF chains cannot form. Equally, the proportion of resorcinol is not sufficiently low for resorcinol to function as a bridge between two methylol groups of separate PF chains. In both cases formation of a very long, continuous polymer chain (the Flory equivalent of a gel) is severely inhibited. Thus, the system cannot gel unless additional formaldehyde hardener is added (which is only added in the glue mix just before use of the adhesive).

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When instead the amount of resorcinol is ≤ 0.411 mol of PF there are not sufficient molecules of resorcinol to function as a bridge between two or three methylol groups of different PF chains. The proportion of resorcinol molecules to achieve this is then insufficient for the gel portion of the system to predominate. Only short linear structures of the type

$$HOCH_2-(Phenol-CH_2)_n-R-CH_2-(Phenol-CH_2)_n-OH$$

are formed. Since the sol fraction is still in the majority, the resin system cannot gel.

(iii) Industrial formulation check: how much resorcinol is used in the best industrial PRF cold-setting adhesive formulations (most of which present a number average degree of polymerization of the original PF resol of approximately 2, and two reactive methylols)? It is interesting that the majority of the industrial PRF adhesives of this type use a PF : resorcinol : molar ratio of 1 : 1.15–1 : 1.17. This is an excess of just 0.08–0.1 mol resorcinol, thus just a small safety margin on what is really necessary to minimize the amount of resorcinol, maintain the adhesive's performance, and avoid gelling. This value has also been obtained over many years by empirical research. For different PRF adhesive formulations one can redo this calculation to account for the different characteristics of the formulation and arrive at an equally correct answer without spending years of empirical research to arrive at an optimized solution.

Exactly the same type of approach can be used for the formulation of other polycondensation adhesives. For example, the formulation of melamine–urea–formaldehyde adhesive resins for wood panel products can also be successfully approached in the same way as has been shown above for the cold-setting PRF adhesives.

B. Determining the Gel Point of an Adhesive Based on a Polycondensation Resin

In the case of the formulation of mixed resins for adhesives for which extensive formulation experience does not exist, the gel theory approach is also particularly useful. Le us examine, as an example, what would be the degree of conversion at the gel point of a resin based on the reaction of resorcinol (R) with acetaldehyde (A) and formaldehyde (F) in relative molar proportions of, respectively, R:A:F = 1:1:0.5. The two aldehydes can react and do react with resorcinol; while under the conditions used they are considered as not being able to react with each other (aldol condensation is indeed minimal under the conditions used to prepare adhesive resins). In short to avoid any gelling of our prereacted resin in the reactor, during manufacture, we want to know at what degree of conversion we can advance reaction of the resin without gelling it.

As the system is relatively complex and presents more than two reagents the simpler approach is to use the formula of Durand and Bruneau (Eq. (10)). This will tell us then that the functionality of resorcinol is 3; the functionality of the two aldehydes in the proportions given is 2 (they are both bifunctional, which simplifies matters), and thus $f_A = 3$ and $f_B = 2$, while $r = (1 \times 3)/(1 \times 2 + 0.5 \times 2) = 1$, to yield according to Eq. (10) $p_{gel} - 1/[1(3-1)(2-1)]^{1/2} = 0.707$ so according to Flory, gel intervenes at 70.7% of the reagent having in fact reacted.

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As we know that Flory's and derived formulas such as Eq. (10) underestimate by approximately 10% the degree of conversion at the gel point one could also use the more exact but more complex Eqs. (18) and (19). In this case Eq. (19) is the one suitable to use. We will then have that $p_{gel} = [(1 + 1 + 0.5)/(1 \times 3 + 1 \times 2 + 0.5 \times 2)] + 1/2(0.5/1)^{1/2} = 0.770$. This indicates that the gel of the system intervenes when 77.0% of the reagents have in fact participated in the reaction, the latter formula yielding a precision of 99.5% while the previous one yields a precision of 91% only.

IV. CONCLUSION

In conclusion, the use of the simpler polymer networking and gel theories constitutes a very useful approach to focus more rapidly and within narrower limits applied formulation research for any polycondensation adhesive resin. This allows much faster adhesive formulation than just the empirical scan research approach still the favorite today for some of these resins. Final experimental verification and adjustments will, however, always be required.

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